DEPARTMENT OF TRANSPORTATION
ENGINEERING SERVICE CENTER
Transportation Laboratory
P. O. Box 19128
Sacramento, California 95819

METHODS OF TEST FOR THE CHEMICAL ANALYSIS OF PORTLAND CEMENT, FLY ASH, POZZOLAN, AND BLENDED CEMENT

CAUTION: Prior to handling test materials, performing equipment setups, and/or conducting this method, testers are required to read "**SAFETY AND HEALTH**" in Part 3 of this method. It is the responsibility of the user of this method to consult and use departmental safety and health practices and determine the applicability of regulatory limitations before any testing is performed.

This test method is divided into the following parts:

1. Determination of Major Constituents of Portland Cement
2. Determination of Chlorides
3. Safety and Health

PART 1. DETERMINATION OF MAJOR CONSTITUENTS OF PORTLAND CEMENT

A. SCOPE

The procedures used in the chemical analysis of portland cement are described in this group of tests. For routine samples, the atomic absorption method is used. For referee samples, or samples where there is a question as to the results, the official methods described in ASTM Designation: C 114 are used.

B. REAGENTS

Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (where such specifications are available).

C. EQUIPMENT

1. Atomic Absorption Spectrophotometer - (AAS) - The Perkin-Elmer Model 2380 AAS has been found to be satisfactory.
2. Carbon and Sulfur Analyzer - The LECO Corp. Model CS225 induction furnace has been found satisfactory.

D. SAMPLE PREPARATION

Before testing, pass samples through a No. 20 sieve in order to mix the sample, break up lumps and remove foreign materials. Discard foreign materials and hardened lumps that do not break up on sieving or brushing. Store the cement in airtight moisture proof containers to prevent aeration or absorption of moisture prior to test.

E. TEST PROCEDURE

1. Wet Chemical Analysis Method:

   For silica, ammonium hydroxide group, aluminum oxide, ferric oxide, calcium oxide, magnesium oxide, sulfur trioxide, ignition loss, insoluble residue, sodium oxide and potassium oxide, follow ASTM Designation: C 114.

2. Rapid Chemical Analysis Method:

   The determination of oxides of silica, aluminum, iron, calcium, magnesium, sodium and potassium using an atomic absorption spectrophotometer and that of sulfur trioxide using the LECO induction furnace are described in the method.

   a. Selection of National Institute of Standards and Technology (NIST) Standards:

      Select a series of at least four standard cement samples that will bracket the expected concentrations of the elements in the unknown samples.

   b. Preparation of Standard Solutions:

      Weigh 0.250 g of NIST standard cement into a 100-mL beaker. Disperse with 20 mL of distilled water and 4 mL of concentrated hydrochloric acid. Break up lumps of cement with a rubber policeman or glass stirring rod, rinse and remove the policeman or rod from the beaker. Cover the sample with a watch glass and digest the sample on a low hot plate for 15 min at approximately 75˚C. During digestion, continuous stir the sample. An oscillating hot plate is preferred for this process. Filter through a medium-texture filter paper into a 200-mL volumetric flask, scrubbing the beaker with a rubber policeman. Wash the sample thoroughly with hot hydrochloric acid (1:99), then with several rinses of hot distilled water. Cool the sample to room temperature, then dilute to a volume of 200 mL. It is recommended that the standard solution be freshly produce each month.

   c. Preparation of Samples:

      Weigh 0.125 g of cement into a 100-mL beaker. Disperse it with 10 mL of distilled water and 2 mL of concentrated hydrochloric acid. Digest and prepare the sample exactly as described in Section 2b, “Preparation of Standard Solutions.” The final filtrate is diluted to a volume of 100 mL.

   d. Preparation of Fly Ash, Pozzolan, and Blended Cement Samples:

      Follow the procedures as described in ASTM Designations: C 311 and C 595, except modify the fusion procedure as follows. A quantity of the ignited sample, equivalent to 0.250 g of the moisture free sample, is mixed with 1.5 g of an equal mixture of $Li_2B_4O_7$ and $LiBO_2$. The fusion procedure is described in ASTM Designation: E 886. The fused mixture is then dissolved in 80 mL of 1:8 hot hydrochloric acid. The resulting solution is filtered and finally diluted to 200 mL. NIST standards for calibration are prepared in the same way.

   e. Standard Solutions:

      Use the standard solutions prepared from NIST standard cements and the instrument parameters and procedures set forth by the manufacturer to calibrate the instrument. Then determine the concentrations of the elements of interest in the test cement samples.

      For the determinations of calcium oxide and magnesium oxide, a portion of the sample solutions prepared in Section 2c are diluted to a proper range with the final dilution containing 0.5 % of lanthanum, which is found to be effective for the suppression of chemical interferences. Standards are diluted similarly.

   f. Sulfur Trioxide Determination Using an Induction Furnace:

      Follow the manufacturer's recommendations. The following has been

found to be a satisfactory method using a LECO induction furnace.

Weigh a 0.15 g sample into a combustion crucible. Add one scoop of Lecocel and one scoop of iron chip accelerator. Follow the instrument manufacturer's directions for this analysis. Standardize the instrument with NIST cement standards using the same procedure as described above.

PART 2. DETERMINATION OF CHLORIDES

A. SCOPE

This part describes a procedure for determining chlorides in portland cement.

B. REAGENTS

Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.

C. EQUIPMENT

1. Chloride specific ion electrode
2. Double junction reference electrode
3. Millivoltmeter compatible with the electrodes

D. TEST PROCEDURES

1. Weigh 2.0 to 5.0 g of portland cement into a 400-mL breaker.
2. Add 100 mL of boiling water.
3. Add a slight excess of 0.1 Normal silver nitrate from a buret (50 mL is an approximate amount of silver nitrate for cement that contains no more than 0.15 % chloride). Record the amount added.
4. Boil the sample for two minutes, remove it from the heat, then cool it slightly.
5. Slowly[1] add 20 mL of nitric acid. Stir and scrub vigorous.[2]
6. Heat and break up any lumps of undissolved cement with the flattened end of a stirring rod, cover the sample and boil it for 2 min.
7. Filter through a medium speed (90-mm "OK" is satisfactory) paper in a Buchner funnel with suction. The filtrate should be clear. Add approximately 1 g of diatomaceous earth to aid filtering if desired.
8. Wash the residue three times with 1:99 nitric acid. Discard the residue.
9. Transfer the filtrate to a 400-mL beaker and cool it to room temperature.
10. Carry three standards through the test procedures with the same amount of acid and silver nitrate but without cement.
11. Adjust all standards and samples to approximately equal volume with distilled water to eliminate blank determination.
12. Titration of Samples:
    a. Titration is required using a ferric ion indicator. With cements that are low in iron, add a few drops of ferric iron indicator (5 g of ferric ammonium sulfate dissolved in 50 mL of 1 Normal nitric acid). Titrate with 0.05 Normal ammonium thiocyanate that has been standardized against the silver nitrate standards to the first permanent red color. Use burets with 0.05-mL graduations and make all readings carefully to the nearest 0.01 mL.

[1] Effervescence often occurs.

[2] A good "scrubber" is made by attaching a small rubber stopper to the end of a glass stirring rod.

b. Titration is required with a specific ion electrode. Following the manufacturer's recommendation for the use of specific ion electrode, titrate the samples with the 0.05 Normal ammonium thiocyanate that has been standardized against the silver nitrate standards prepared in Step 10. Plot a curve of the change in potential against volume of thiocyanate to find the end point.

E. CALCULATIONS

Calculate chlorides as chlorine (Cl) by the following formula:

% Chlorine = [(A x N) - (B x M)] x F x 100 / mass of the sample, to the nearest 1g

Chlorine (ppm) = % x 10 000

Where A = mL of $AgNO_3$
N = Normality of the $AgNO_3$
B = mL of NH_4SCN
M = Normality of the NH_4SCN
F = conversion factor to Cl, or 0.03546

PART 3. SAFETY AND HEALTH

This method may involve hazardous materials, operations and equipment. This method does not purport to address all the safety problems associated with its use. It is the responsibility of whomever uses this method to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. This method involves the handling of hazardous chemicals and samples, compressed and flammable gases, and sophisticated instruments which can be dangerous.

Prior to handling testing or disposing of any waste materials, testers are required to read:

1. Caltrans Laboratory Safety Manual

2. Safety precautions as outlined in California Test 400.

These guidelines pertain to requirements for general safety principles, standard operating procedures, protective apparel, disposal of materials and how to handle spills, accidents, emergencies, etc. Testers are mandated to always observe good hygiene practices. Wash hands after handling samples and before eating, drinking or smoking. Users of this method do so at their own risk.

REFERENCES:

California Test 400
ASTM Designation: C 114
AASHTO Designation: T 105
Portland Cement Association, Research Department Bulletin 214, "Analysis of Portland Cement by Atomic Absorption."

End of Text (California Test 404 contains 4 pages)